

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) INFORMATION RECORDING

(71) We, AMERICAN CYANAMID COMPANY, a corporation organised and existing under the laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of recording information and a coding ink suitable for use in this method. More particularly, the present invention is an improvement in the recording process and coding ink described and claimed in our Patent No. 1143362.

The main patent describes and claims a process of recording information by applying to a substrate one or more symbols derived in accordance with a predetermined code, wherein at least one symbol is formed by applying to an area of the substrate at least two luminescent substances capable of emitting radiation in discrete, predetermined and mutually different frequency bands when illuminated with short wavelength radiation, at least one of said luminescent substances being a complex of a rare earth metal ion having atomic number greater than 57.

Further, the main patent describes and claims a coding ink suitable for use in this recording process, the coding ink comprising a mixture of at least two luminescent substances capable of emitting radiation in discrete, predetermined and mutually different frequency bands when illuminated with short wavelength radiation, at least one of said luminescent substances being a complex of a rare earth metal ion having an atomic number greater than 57; and a carrier for said mixture.

[Price 25p]

An important advantage of the information recording process of the main patent is that the coding of symbols is independent of any shape and can, if desired, be entirely invisible and therefore secret.

One of the problems is efficiency of photoluminescence for certain kinds of substrates. The problem may be considered as analogous to the signal-to-noise ratio in electronic operations, that is to say, the intensity of the desired signal as compared with responses which are spurious. With ordinary substrates, such as white paper, very satisfactory results can be obtained. However, when very thin films of luminescent materials are used, which may be 10 microns or less, in thickness on substrates which absorb the short wavelength exciting radiation very strongly, the effective path lengths through the thin film are so short that the signal-to-noise ratio can be adversely affected. When thin films of photoluminescent material are used for label marking and the like, there is never an excess of photoluminescence energy with ultraviolet radiation of modest powers, and the same difficulty with very thin films on radiation absorbing substrates is encountered.

The present invention seeks to increase the reliability of detection of photoluminescence, particularly on radiation absorbing substrates, in the recording process of the main patent.

According to the present invention, the information recording process of the main patent is improved by the formation on said substrate of at least one symbol containing, in addition to said luminescent substances, a finely divided material having a refractive index substantially different from that of any of said luminescent substances for effecting scattering of said short wavelength radiation.

According to a further aspect of this invention, the coding ink of the main patent is improved by the presence in the ink of a

5 finely divided particulate material having a refractive index substantially different from that of any of said luminescent substances in the ink, whereby upon irradiation with said short wavelength radiation of a symbol formed from the ink on a substrate said radiation is scattered by said particulate material.

10 It is usually preferred that the materials which are used in accordance with the present invention to effect scattering of the short wavelength radiation used to excite the luminescent components should exhibit substantially no absorption of either the exciting radiation or of the photoluminescence.

15 The scattering material may be in the form of solid particles, in which case it usually has a refractive index greater than that of the luminescent substances. Alternatively, the scattering material may be in the form of gas bubbles, for example bubbles of nitrogen, distributed throughout the luminescent substance. In this case the materials (and for the purposes of this invention the gas in bubbles is considered as a material) usually have refractive indices very much lower than that of the luminescent substances.

20 Scattering material in the form of gas bubbles may be readily provided by incorporating into the coding ink from which the coded symbols are to be formed a substance which will generate gas bubbles of the required properties, e.g. nitrogen gas bubbles, upon heating of the symbols.

35 When the scattering materials are finely divided solids, they may scatter radiation both exciting and photoluminescent, and under visible light such materials usually appear as white or faintly colored pigments. Gas bubbles, on the other hand, may or may not appear as white pigments under visible light, depending on their size. They do however, in every case scatter shortwave exciting radiation, such as ultraviolet.

45 Some of the best scattering material is substantially transparent to ultraviolet light. An example is finely divided magnesium oxide or, of course the gases, such as nitrogen, in bubbles. Some materials are excellent scatterers for visible radiation, such as the white pigment  $\text{TiO}_2$ , but this is not in every case ideal because it also absorbs strongly in the ultraviolet region at 3130 Å, but not as much at longer wavelengths, such as 3650 Å. Even for the shorter radiation a small amount of  $\text{TiO}_2$  may improve results by reason of its very strong scattering effect, whereas a larger amount, which would produce quite substantial absorption, can actually decrease the effectiveness of the photoluminescence. In all cases the amount of scattering material may vary. It is not particularly critical even in the case of such materials as  $\text{TiO}_2$ , but an excessive amount can, of course, mask photoluminescent light even though it is not a strong absorber for ultraviolet light. In general, therefore, the

amount to be used is sufficient to effect high scattering of radiation but below that at which luminescent radiation efficiency is significantly reduced. In general, the percentage is quite moderate and will vary from a few percent up to 20% or 40%. However, amounts up to 60% can be used in certain cases.

70 While the present invention is useful with thin films of photoluminescent substances on any substrate, the percentage effect is much greater with absorbing substrates. On a black substrate, the scattering material can give an increase in efficiency of photoluminescence of fourfold, in spite of the fact that the substrate absorbs exciting radiation practically 100% and does not reflect any significant amount of visible radiation.

85 The present invention is of great practical utility because many substrates, such as Kraft paper and other strongly absorbing substrates, are very frequently used for containers and other articles which must be labeled by photoluminescent designs or coded inks. It has made possible the use of photoluminescent marking or coding using the teachings of the main patent with a number of materials where the reliability in the past has been marginal.

90 The thickness of the photoluminescent symbol varies but is often in the range of 1.0 to 20 microns. Thinner symbols are known, and of course the effect of the present invention is lost with very thick symbols where the absorption of the exciting radiation reaches a high percentage even without the addition of scattering material. In general, symbol thicknesses significantly in excess of 100 microns and containing appreciable amounts of luminescers in particulate form do not show sufficiently great increases in photoluminescence to make the additive worthwhile. This is no real practical drawback as such thick symbols are practically never used.

105 The invention will now be described further with reference to the accompanying drawings, in which:

Figure 1 is a cross-section through a symbol of the prior art, and

115 Figure 2 is a similar cross-section through a symbol formed in accordance with the present invention.

120 The two figures of the drawings show cross-sections through photoluminescent symbols on substrates. The thickness is very grossly exaggerated for clarity. Figure 1 represents the prior art, a dark substrate being shown at (1) with the thin symbol, for example 1—20 microns, at (2), and three arrows (3) representing the short, direct paths of radiation when the symbol is irradiated with ultraviolet light. For simplicity it will be assumed that the radiation is normal to the substrate. The paths are very short, and as the strongly absorbing substrate (1) reflects little ultra-

violet light, the amount of actual irradiation of the photoluminescent components in the short radiation paths is drastically reduced. Figure 2 shows a similar symbol according to the present invention, with substrate and symbol bearing the same reference numerals. A number of particles of different refractive index are shown at (4), again of course grossly exaggerating the particle size for clarity. A short path of radiation is shown at (3), which can be compared with a much longer path represented by the broken arrow (5) due to scattering by the particles of the scattering material.

The invention will also be described in conjunction with the following experiments, in which the parts are by weight unless otherwise described. In these experiments, the coding ink which is formed contains only one luminescent substance, but nevertheless the experiments do clearly demonstrate the advantages of the present invention. In order to obtain accurate comparisons, all of the experiments were drawdowns of a polymethacrylate film containing the photoluminescent materials and, where present, the scattering agent. The films were all in the 15 to 20 micron range in thickness and were prepared using a solution made by dissolving 35 gr. polymethylmethacrylate in 65 gr. of benzene. The photoluminescent material and scattering material (hereinafter termed "filler") were added to the polymer solution in the amounts specified in the examples, the substrate was stretched out on a hard surface, such as plate glass, a ribbon of the polymer solution was poured onto the paper and then it was drawn out into a film with a doctor blade. The film was then allowed to dry and was irradiated with a standard ultraviolet lamp filtered to emit only the 3130 Å line of mercury, the photoluminescence being detected by a suitable detector for the wavelength band of the luminescence, which detector transformed luminescent radiation into electric current, which was measured on a microammeter. This setup permitted accurate quantitative evaluations of the effects of the present invention.

#### Experiment 1

A drawdown was made on white bond paper, the polymethylmethacrylate film containing 5% of the complex europium tris trifluoroacetylacetonate and two equivalents of a synergic agent, trioctyl phosphine oxide. On irradiation with ultraviolet light a current of 25  $\mu$ a was noted. A second drawdown in which a small amount, 2% by weight of the film, of finely divided titanium dioxide pigment was dispersed showed a current of 30  $\mu$ a. When a second drawdown was made on mat black paper, the current was 25% as strong as on the white paper, which is an unexpected result.

#### Experiment 2

Drawdowns were made on black photographic film. The polymethylmethacrylate film contained 2.56% yttrium vanadate doped with europium and 2.8% of white pigment, (coprecipitate of alumina and barium sulfate). The current was 0.26  $\mu$ a. A second drawdown with 1.76% of the yttrium vanadate-europium complex and 20.7% of the white pigment gave a current of 1.0  $\mu$ a.

#### Experiment 3

Drawdowns were made on Kraft multiwall paper utilizing the photoluminescent components listed below at the percentage levels indicated. Then the indicated amounts of yttrium oxide,  $Y_2O_3$ , as scattering filler were mixed with the luminescer dispersions and drawdowns were made on the same type of Kraft paper. The ratios of luminescent signal with the added  $Y_2O_3$  filler to signal without the filler are given below.

		Signal Ratio
0.56% Eu	7.02% $Y_2O_3$	1.53
4.2% Tb	4.0% $Y_2O_3$	2.30
1.07% Dy	6.65% $Y_2O_3$	1.67

#### Experiment 4

Drawdowns were prepared using 0.9% of the luminescer dysprosium doped YVO<sub>4</sub> in the polymer solution, and also using 29% of various scattering additives. The ratios of luminescence signal with the additive to luminescence signal without the additive are given below for two different substrates, one a Kraft multiwall paper and the other a white tape used for labeling laboratory bottles. Irradiation was predominantly at 3130 Å.

Filler	Signal Ratio	
	Kraft	White Tape
TiO <sub>2</sub>	0.25	0.1
BaSO <sub>4</sub>	1.8	1.3
NaCl	1.3	1.1

This experiment, when compared to Experiment 1, illustrates a point which has been referred to above, that with certain scattering materials, such as TiO<sub>2</sub>, which are also absorbers in the ultraviolet or in certain wavelength bands thereof, an improvement may be obtained with a small amount of the scattering material, but results are poorer with a larger amount. The improvement in Experiment 1 has 2% TiO<sub>2</sub>, which is not sufficient to absorb a major portion of the ultraviolet light. However, in Experiment 4 the amount is 29%, which is so great that the absorbing factor becomes more important than the scattering effect. As a result, in the above table the signal ratio is less with a large amount of TiO<sub>2</sub> than with no particulate matter at all. The fact that the decrease in effectiveness is somewhat less on the dark substrate repre-

5 sented by Kraft paper than on the white tape is due to the fact that with no particulate matter the white tape gives off a much stronger luminescence, because the white tape, of course, was a good diffuse reflector, than in the case of the Kraft paper. Therefore, when there was a drastic absorption of ultraviolet light, this reduced the brighter photoluminescence from the white tape to a greater degree than the smaller luminescence on the Kraft paper.

#### Experiment 5

15 Four drawdowns were made to europium-yttrium vanadate complex as a photoluminescer and of a filler of finely divided silica, under the name "Cab-O-Sil". The results were as follows:

	% Eu Luminescer	% Filler	Signal Ratio
	1.06	2.7	1.08
20	1.12	7.5	1.05
	2.12	19	2.00

#### Experiment 6

25 The procedure of Experiment 5 was repeated replacing the silica with various amounts of finely divided magnesium oxide. The results were as follows:

	% Eu Luminescer	% Filler	Signal Ratio
	1.05	4	1.13
	1.03	11.7	1.28
30	1.0	16.9	1.93
	1.08	20.4	2.80
	0.8	29	6.00
	1.0	42	5.10

#### Experiment 7

35 The procedure of Experiment 5 was repeated with varying amounts of finely divided barium sulfate as a filler. The results are as follows:

	% Eu Luminescer	% Filler	Signal Ratio
40	1.0	9.4	1.14
	1.15	18.5	1.10
	1.12	24.2	1.55
	1.0	35.5	2.40
	1.0	46	3.35
45	0.85	49.5	4.60
	1.04	59.3	3.90

#### Experiment 8

The procedure of Experiment 5 was repeated but the filler was yttrium oxide,

	Photoluminescer	Scatterer	Current	Signal Ratio
	1.35%	None	111 $\mu$ a	
	1.48%	1.7% MgO	145 $\mu$ a	1.31
105	1.38%	3.10	150 $\mu$ a	1.35
	1.48%	10.5	186 $\mu$ a	1.67
	1.31%	45	235 $\mu$ a	2.12

Y<sub>2</sub>O<sub>3</sub>, which is transparent to ultraviolet light. The results are as follows:

% Eu Luminescer	% Filler	Signal Ratio
1.05	4.62	1.06
1.02	10.2	1.35
0.83	14.1	2.00
1.09	17	1.82
0.92	26	3.00
1.17	58	6.40

#### Experiment 9

A drawdown of a 35% solution of polymethylmethacrylate in benzene was made on Kraft paper using a 0.0915" draw knife. The film contained 8.8% of azobisbutyronitrile and 1.14% of europium doped yttrium vanadate complex as a photoluminescent material. The photoluminescer was the same as the one used in Experiment 2, but, as will be seen, the proportion in the film was somewhat less. The sample was split into two samples and one-half was heated to a temperature sufficiently high to decompose the azobisbutyronitrile, forming closed cells of nitrogen gas. The other half was not heated and constituted a control. The surface of the heated sample turned milky white as a result of the nitrogen filled bubbles. When tested as described in the preceding experiments, the luminescent intensity of the untreated piece was 9.5  $\mu$ , while the intensity of the heated example was 16  $\mu$ . The signal ratio was, therefore, approximately 1.7.

This experiment illustrates a situation where the finely distributed materials, bubbles filled with nitrogen, had a refractive index much less than that of the polymethylmethacrylate instead of a greater refractive index, as in the case of the solid particulate matter in the preceding experiments.

#### Experiment 10

The effect of scattering on an organic broad band photoluminescent material was tested. The photoluminescent material was 2 - (2 - hydroxyphenyl) - 6 - chloro - 4 - (3H) - quinazalone. The film was the same as in Experiment 1 and varying amounts of photoluminescer, and in the samples having scattering material, magnesium oxide, were tested. Irradiation was with ultraviolet light at 3130 Å. The following table shows the results; for compactness the particular photoluminescent material is referred to as photoluminescer:

Photoluminescer	Scatterer	Current	Signal Ratio
1.35%	None	111 $\mu$ a	
1.48%	1.7% MgO	145 $\mu$ a	1.31
1.38%	3.10	150 $\mu$ a	1.35
1.48%	10.5	186 $\mu$ a	1.67
1.31%	45	235 $\mu$ a	2.12

The above experiment shows that the enhancement by the scattering with magnesium oxide was effective with a broad band organic fluorescer just as in the preceding experiments with narrow band fluorescing chelates. The particular material which fluoresces in the green is only a typical example of the type of organic fluorescers which are described in British Patent 1,025,435, French Patent 1,416,618 or Japanese Patent 535,787 (1968).

Apart from the concomitant use of a scattering material with the luminescent substances, the recording process of this invention may be carried out as described in Patent No. 1,143,362, to which the reader is directed for details concerning the preferred luminescent substances, etc.

#### WHAT WE CLAIM IS:—

1. An improvement in the process of recording information defined in Claim 1 of Patent No. 1143362, the improvement comprising the formation on said substrate of at least one symbol containing, in addition to said luminescent substances, a finely divided material having a refractive index substantially different from that of any of said luminescent substances for effecting scattering of said short wavelength radiation.
2. A process according to Claim 1 wherein said finely divided material exhibits substantially no adsorption of said short wavelength radiation or of said radiations emitted by said luminescent substances upon illumination with said short wavelength radiation.
3. A process according to Claim 1 or Claim 2, wherein said finely divided material is finely divided particulate material having a refractive index substantially greater than that of any of said luminescent substances.
4. A process according to Claim 3, wherein said finely divided material is  $\text{TiO}_2$ ,  $\text{BaSO}_4$ ,  $\text{NaCl}$  or  $\text{MgO}$ .
5. A process according to Claim 1 or Claim 2, wherein said finely divided material is gas bubbles.
6. A process according to Claim 5, wherein said gas is nitrogen.

7. An improvement in the cooling ink defined in Claim 9 of Patent No. 1143362, the improvement comprising the presence in the ink of a finely divided particulate material having a refractive index substantially different from that of any of said luminescent substances in the ink, whereby upon irradiation with said short wavelength radiation of a symbol formed from the ink on a substrate said radiation is scattered by said particulate material.

8. A coding ink according to Claim 7, wherein said particulate material exhibits substantially no absorption of said short wavelength radiation or of said radiation emitted by said luminescent substances upon illumination with said short wavelength radiation.

9. A coding ink according to Claim 7 or Claim 8, wherein said particulate material is  $\text{TiO}_2$ ,  $\text{BaSO}_4$ ,  $\text{NaCl}$  or  $\text{MgO}$ .

10. The coding ink defined in Claim 7 modified in that the finely divided particulate material is replaced by a substance which upon heating of a symbol formed from the ink on a substrate generates gas bubbles within the symbol which have the refractive index properties defined in Claim 7 for the particulate material.

11. A coding ink according to Claim 10, wherein nitrogen bubbles are generated upon heating of the symbol.

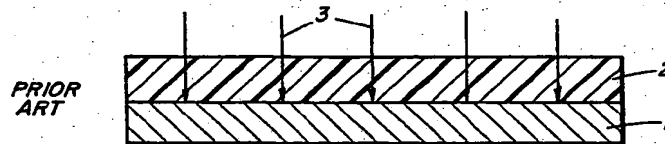
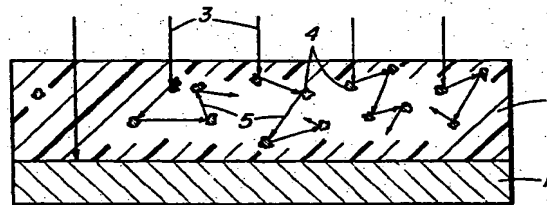
12. A coding ink according to Claim 7 or Claim 10 and substantially as hereinbefore described.

13. An information recording process according to Claim 1 and substantially as hereinbefore described.

14. A substrate bearing information recorded by a process according to any one of Claims 1—6 or Claim 13.

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**FIG. 1****FIG. 2**